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(71) Applicant *(for all designated States except US)*: MICROSYSTEM DESIGN SPECIALISTS LIMITED [GB/GB]; Churchill House, 29 Mill Hill, Pontefract, West Yorkshire WF8 4LD (GB).

(71)(72) Applicant and Inventor: FOLLER, Peter, C. [US/US]; 2000 Commonwealth Avenue, Unit 1110, Brighton, Boston, MA 02135 (US).

(74) Agent: HARRISON, Michael, Robert; Dibb, Lupton, Broomhead and Prior, 117 The Headrow, Leeds LS1 5JX (GB).

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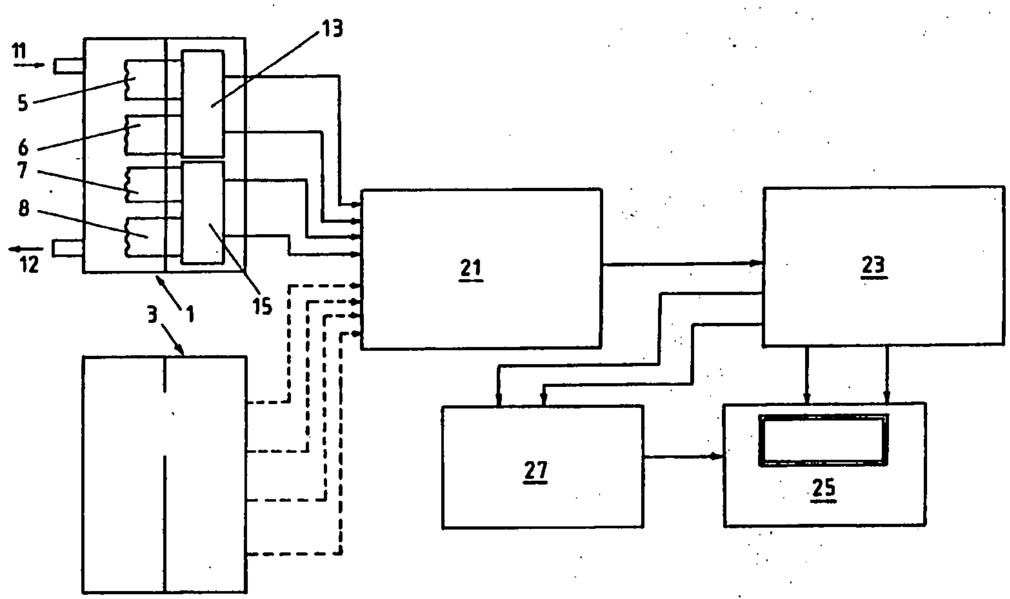

(57) Abstract

Apparatus for detecting and monitoring a component of a gaseous mixture, the component being a gas such as ozone or chlorine oxide which is capable of exothermic decomposition under the influence of a catalyst, includes a device (1) defining a flowpath for the gasesous mixture within which is located a catalyst for decomposing the component and an electrical element (6) having an electrical property which varies with the temperature of the element. The apparatus includes means (21, 23, 25 and 27) for processing the output electrical signals from the device and for displaying information relating to the amount of the component in the gaseous mixture.

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GAS MONITOR

This invention relates to apparatus and methods for the detection and monitoring of one or more components of a gaseous mixture and more particularly to a gaseous mixture. By way of examples, components of gaseous mixtures with which this invention is concerned include ozone and chlorine dioxide. Although reference will be made hereinbelow mainly to ozone monitors, it should be understood that the invention is applicable to other gases such as chlorine dioxide.

Ozone monitors are of use in various processes in which the gas ozone is used. Examples of such processes are the treatment of effluent in sewerage-treating facilities, purification of water which has been used in various chemical processes, the purification of bottled or potable water, the sterilisation of materials used in the medical and pharmaceutical industries, in the food industry (for instance, ozone is used to prolong the period for which seafoods remain fresh) and in the electronics industry, particularly the production of semi-conductors, where the highest level of contamination-free water is required. In these and other processes, it is normally required to know the amount of ozone produced by an ozone-generator prior to the gas stream being fed to the material being treated and also, very often, the amount of ozone in the gas exiting from the material

being treated. Indeed, it may be desired to monitor the ozone level at various points along the flowpath of the gas containing the ozone.

Apparatus for monitoring the presence of ozone in a gas stream may provide information relating to such matters as ozone mass flow, ozone mass-flow rate, gas stream flow rate and ozone concentration. Conventional ozone monitors incorporate amperometric or potentiometric electrochemical cells or may be in the form of ultra-violet spectrophotometers or be concerned with the measurement of the photochemical reaction of ozone with ethylene. Aqueous-phase electrochemical sensors have proved unreliable since their electrodes and membranes are easily fouled, their internal solutions may become contaminated and the maintenance of the apparatus requires complex disassembly. The accuracy of such apparatus is low. Ultra-violet spectrophotometers are expensive, require a reference gas, and incorporate optics which may easily become misaligned. They also require moving parts in the form of solenoid valves. In addition, the ultra-violet spectrum of ozone may be confused with that of other compounds present in the gas being monitored. The photochemical approach is less common due to the need for a continuous supply of reagents and the ability to handle the exhaust products.

According to the present invention, there is provided apparatus for detecting or monitoring a component of a gaseous mixture, the component being capable of exothermic decomposition under the influence of a catalyst, the apparatus comprising:

- means for feeding the gaseous mixture along a flowpath;
- a catalyst support member located in said flowpath and having a catalyst supported thereon;
- temperature-responsive means located in said flowpath and forming part of an electric circuit for producing an electrical output relating to the temperature of said temperature-responsive means; and
- means for processing said output and displaying information relating to the amount of the component in the gaseous mixture.

The component may, for instance, be ozone or chlorine dioxide or may itself be a mixture of exothermically decomposable gaseous components.

The temperature-responsive means may be any suitable device having an electrical property which varies with temperature, an example being a thermocouple which responds to temperature change by a change in the voltage which the thermocouple generates. Preferably, the temperature-responsive means is a device whose resistance varies with temperature. Such a device will be referred to hereinafter as a resistance-temperature-measuring

device, or RTD. An RTD may, for instance, be a thermistor, a bolometer or a platinum-resistance thermometer. A platinum-resistive temperature device is preferred for the present invention since it gives a good linear response over a wide temperature range.

The catalyst may be any suitable catalyst which is capable of exothermically decomposing the component of the gas stream being monitored. Ozone decomposing catalysts include cobalt oxide, Hopkalite and dispersed platinum. A preferred material is manganese dioxide. The metal in manganese dioxide is in its highest oxidation state and does not catalyse the decomposition of other materials which may be present in the gas flow.

Apparatus in accordance with the present invention is capable of providing information relating to the concentration and mass-flow of ozone as well as the mass-flow rate of the gas stream which contains the ozone. The accuracy of the apparatus is high, typically of the same order of known commercial mass-flow transducers, that is to say, within 1% to 2%. There are no moving parts in the apparatus, and the maintenance required is minimal.

A platinum-resistance thermometer device, used in the present invention, may be provided encapsulated in a glass or ceramic housing. Preferably, the catalyst is located on the external

surface of such a device. The catalyst may be deposited on this external surface which is first pre-treated to make it more receptive to the application of the catalyst. Preferably, a wash-coat in the form of an aqueous slurry is first applied to the surface. The slurry may be a dispersion of oxide materials, including alumina, in aqueous acetic acid. The encapsulated RTD may be dipped into such a slurry in order to coat it. Glass or ceramic-encapsulated RTDs can be etched with hydrofluoric acid before being dipped in the slurry in order to improve adherence. Once dipped, the RTD may be heat-treated or fired at a temperature in excess of 300°C to provide a highly receptive surface with a large surface area onto which the catalyst itself may then be applied. Application of the manganese dioxide catalyst to the wash-coat on the surface of the RTD housing may be carried out by thermal decomposition of the chloride or nitrate salt of manganese. The wash-coated RTD element may be repeatedly dipped into a solution of the salt and then heated in air to a temperature in excess of 200°C. After a sufficient number of coating steps, the final firing in air to a temperature greater than 350°C affords a suitable and reproducible catalytic surface. Other catalytic materials such as platinum, cobalt oxide and Hopkalite can be applied to an RTD in a similar fashion. Powders of catalytic materials may alternatively be applied to an RTD by sintering with alumina or the plastics PDVF, FEP, TFE or TEF-PFA.

The present invention also provides a temperature-responsive catalytic device for use in the detection or monitoring of a component of a gaseous mixture, the device comprising temperature-responsive means having an electrical property whose value varies with the temperature of the device, encapsulation means encapsulating said temperature-responsive means and, located on the external surface of said encapsulation means, a catalyst capable of catalysing the exothermic decomposition of said component.

The present invention further provides a sensing head including the temperature-responsive device of the present invention together with one or more further temperature-responsive means and connection means for connecting the sensing head to means for processing the electrical outputs from said sensing head.

The present invention also provides a method for detecting or monitoring a component of a gaseous mixture, the component being capable of exothermic decomposition under the influence of a catalyst, the method comprising:

- feeding the gaseous mixture along a flowpath within which is located a catalyst for effecting exothermic decomposition of said component;
- allowing said gaseous mixture to contact the catalyst to effect exothermic decomposition of the component;

- causing the heat generated by said exothermic decomposition to raise the temperature of the temperature-responsive means located in said flowpath thereby to vary the electrical output of a circuit of which the temperature-responsive means forms a part; and
- feeding said electrical output to processing means for processing said output and displaying information relating to the amount of the component in the gaseous mixture.

An embodiment of the present invention will now be described, by way of example only, and with reference to the accompanying drawings, in which:

- Figure 1 is a schematic diagram showing the entire apparatus; and
- Figure 2 is a diagram showing in detail an RTD of use in the apparatus of Figure 1.

Referring to Figure 1 of the accompanying drawings, apparatus in accordance with the present invention includes one or more sensing heads 1,3, each of which contains a plurality of resistance-temperature-measuring devices (RTDs), such as 5 - 8 within sensing head 1. These RTDs form part of an electrical circuit the outputs of which are fed to a monitor which includes all the components shown in Figure 1 to the right of the sensing heads.

Referring in detail to sensing head 1, this sensing head is provided with a gas stream inlet 11 and a gas stream outlet 12, the gas stream within sensing head 1 being caused to pass over the various RTDs located within the head. RTDs 5 and 6 form part of a first electrical circuit 13. RTD 5 is coated with an ozone decomposing catalyst, specifically manganese dioxide, and RTD 6 is a similar device but not carrying the catalytic coating.

A second electrical circuit 15 includes RTDs 7 and 8, the former being heated by means of an electrical current caused to flow through it and the latter being unheated. Neither of these RTDs is coated with catalytic material. As will be described in further detail below, the RTDs are located within sensing head 1 such that the gas flows sequentially over each RTD. In an alternative embodiment of the present invention, the sensing head may be arranged such that the RTDs lie in parallel flowpaths within the sensing head.

In use, gas entering the sensing head 1 will cool the heated RTD 8, which is the last RTD in the flowpath. As a result, this RTD will have its electrical resistance altered. The electrical output from circuit 15 can be processed to produce information relating to the gas-stream flow.

Exothermic decomposition of ozone on the catalytic surface of RTD 6 causes the temperature of the RTD to rise and the resistance to alter. The output from circuit 13 which, in effect, compares the resistance of RTD 6 with the reference RTD 5 may be processed to provide information relating to the concentration of ozone in the gas stream.

The above-referred to monitor includes circuitry represented by block 21 for effecting analogue-to-digital conversion of the outputs of the or each sensing head. The resulting digital representations of the resistance readings are fed to circuitry represented by processing unit 23 which converts resistance data to flow and concentration data. This data is fed directly to display device 25 where it can be displayed in the form of concentration (weight % of ozone in the gas stream) and flow (litres per/hr of the gas stream). The same data is also fed to circuitry represented by block 27 which calculates the mass flow and feeds the resultant data to display device 25 where it is displayed in terms of the amount of ozone in the gas stream (gm/hr).

Preferably, the apparatus includes an extensive digital memory allowing accurate calibration of the instruments. The digital electronics can use the calibration data to combine the mass-flow and flow rates to determine a total mass-flow rate giving a complete gas stream audit.

Referring to Figure 2 of the accompanying drawings, a sensing head, such as that indicated by 1 in Figure 1, includes a body which is formed from three separate PVC mouldings 31, 33 and 35. They are connected together by means of fixing bolts (not shown) passing through the three components and secured by locating nuts which are positioned in milled grooves 37 located in component 31. The sensing head may be secured to, for instance, a bulkhead by means of bolts passing through bores 39 in component 31.

The sensing head body described above defines a flowpath 41 indicated by arrows. Flowpath 41 extends from threaded inlet point 43 to a similarly threaded outlet point 45. As illustrated in Figure 2, the flow path extends mainly through the middle component 33 of the sensor body. It follows an essentially rectangular-wave shaped path within which are located the four RTDs 5, 6 7 and 8. Each RTD is located in a part of the flowpath which extends parallel of the longitudinal axis of the sensing head. It lies mainly within central component 33 but extends a short distance into upper component 35. Electrical connection extends from that end of the RTD located in upper component 35 via wire 51 through upper component 35 to the exterior of the sensing head.

Apart from the inlet 43 and outlet 45, the flowpath 41 is located mainly within middle component 33 and is effectively closed by

means of lower and upper components 31 and 35. The three body components are sealed together by means of a silicon-based sealant.

The above-described sensing head is particularly suitable for dealing with very low flow rates. The length-wise flow along the RTDs is more uniform than would be the case with a cross-flow. The particular sequence of the RTDs within the sensing head is not important except that it is preferred that the electrically heated RTD 8 should be the last RTD in the flow path. In this way, the sensing head may be kept as isothermal as possible.

The above-described apparatus may be used to monitor any concentration of ozone, from a concentration of the order of a few parts per million up to the safety limits for ozone in contact with catalytic surfaces which might be of the order of 10 to 15 weight %.

CLAIMS

1. Apparatus for detecting or monitoring a component of a gaseous mixture, the component being capable of exothermic decomposition under the influence of a catalyst, the apparatus comprising:
   - means for feeding the gaseous mixture along the flowpath;
   - a catalyst support surface located in said flowpath and having a catalyst supported thereon;
   - temperature-responsive means located within said flowpath and forming part of an electric circuit for producing an electrical output relating to the temperature of said temperature-responsive means; and
   - means for processing said output and displaying information relating to the amount of the component in the gaseous mixture.

2. Apparatus in accordance with Claim 1 in which the component is ozone or chlorine dioxide.

3. Apparatus in accordance with Claim 1 or Claim 2 in which the temperature-responsive means is a device whose resistance varies with the temperature of the device.

4. Apparatus according to Claim 3 in which the device is a platinum resistance temperature device.

5. Apparatus according to the any of the preceding claims in which the catalyst is manganese dioxide.

6. Apparatus according to any of the preceding claims in which the temperature-responsive device is encapsulated in a glass or ceramic housing.

7. Apparatus in accordance with Claim 6 in which the catalyst is located on the external surface of the housing.

8. A temperature-responsive catalytic device for use in the detection or monitoring of a component of a gaseous mixture, the device comprising temperature-responsive means having an electrical property whose value varies with the temperature of the device, encapsulation means encapsulating said temperature-responsive means and, located on the external surface of said encapsulation means, a catalyst capable of catalysing the exothermic decomposition of said component.

9. A sensing head including a temperature-responsive device according to Claim 8 together with one or more further temperature-responsive means and connection means for

connecting the sensing head to means for processing the electrical outputs from said sensing head.

10. A method for detecting or monitoring a component of a gaseous mixture, the component being capable of exothermic decomposition under the influence of a catalyst, the method comprising:

- feeding the gaseous mixture along a flowpath within which is located a catalyst for effecting exothermic decomposition of said component;
- allowing said gaseous mixture to contact the catalyst to effect exothermic decomposition of the component;
- causing the heat generated by said exothermic decomposition to raise the temperature of the temperature-responsive means located in said flowpath thereby to vary the electrical output of a circuit of which the temperature-responsive means forms a part; and
- feeding said electrical output to processing means for processing said output and displaying information relating to the amount of the component in the gaseous mixture.

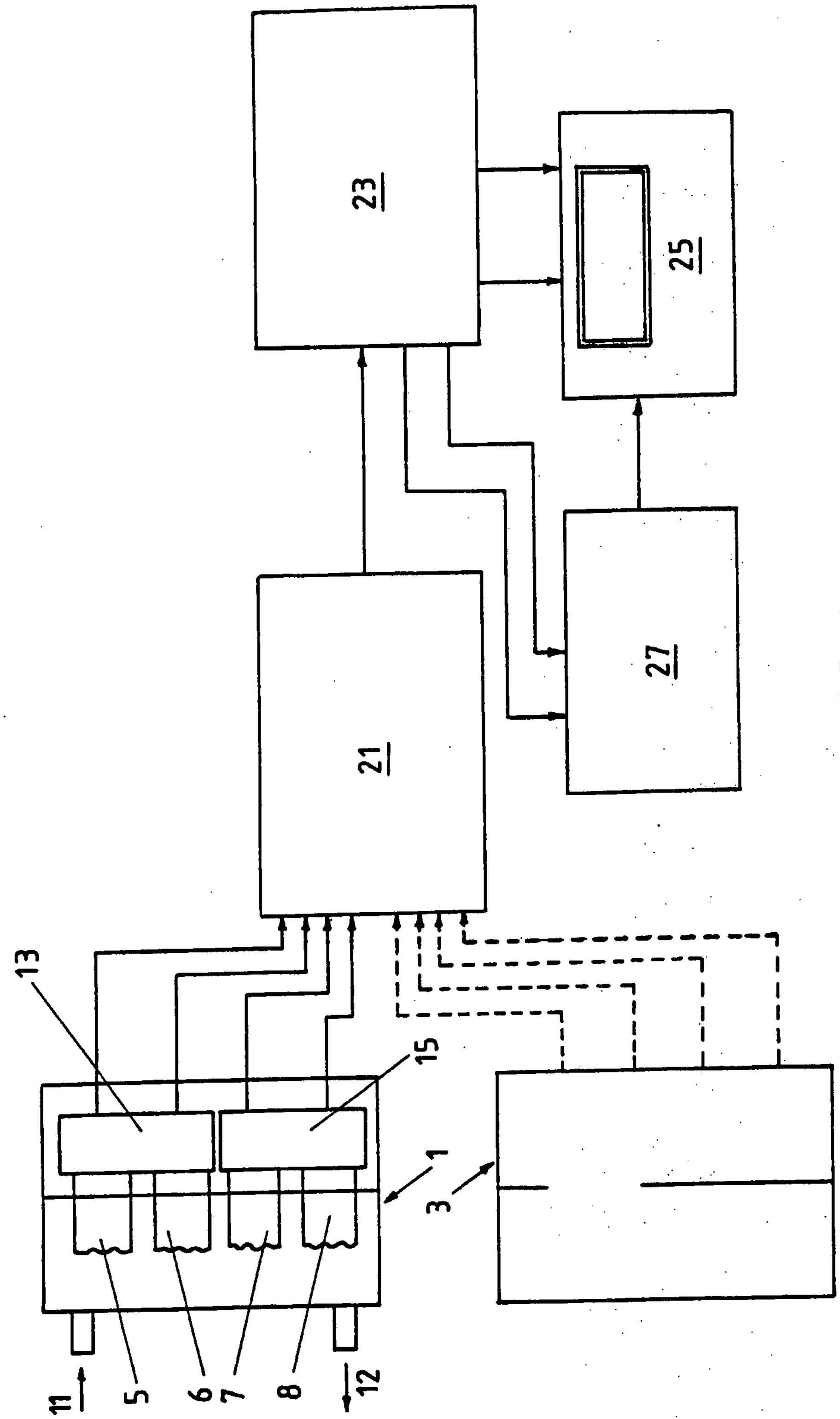

FIG. 1

SUBSTITUTE SHEET

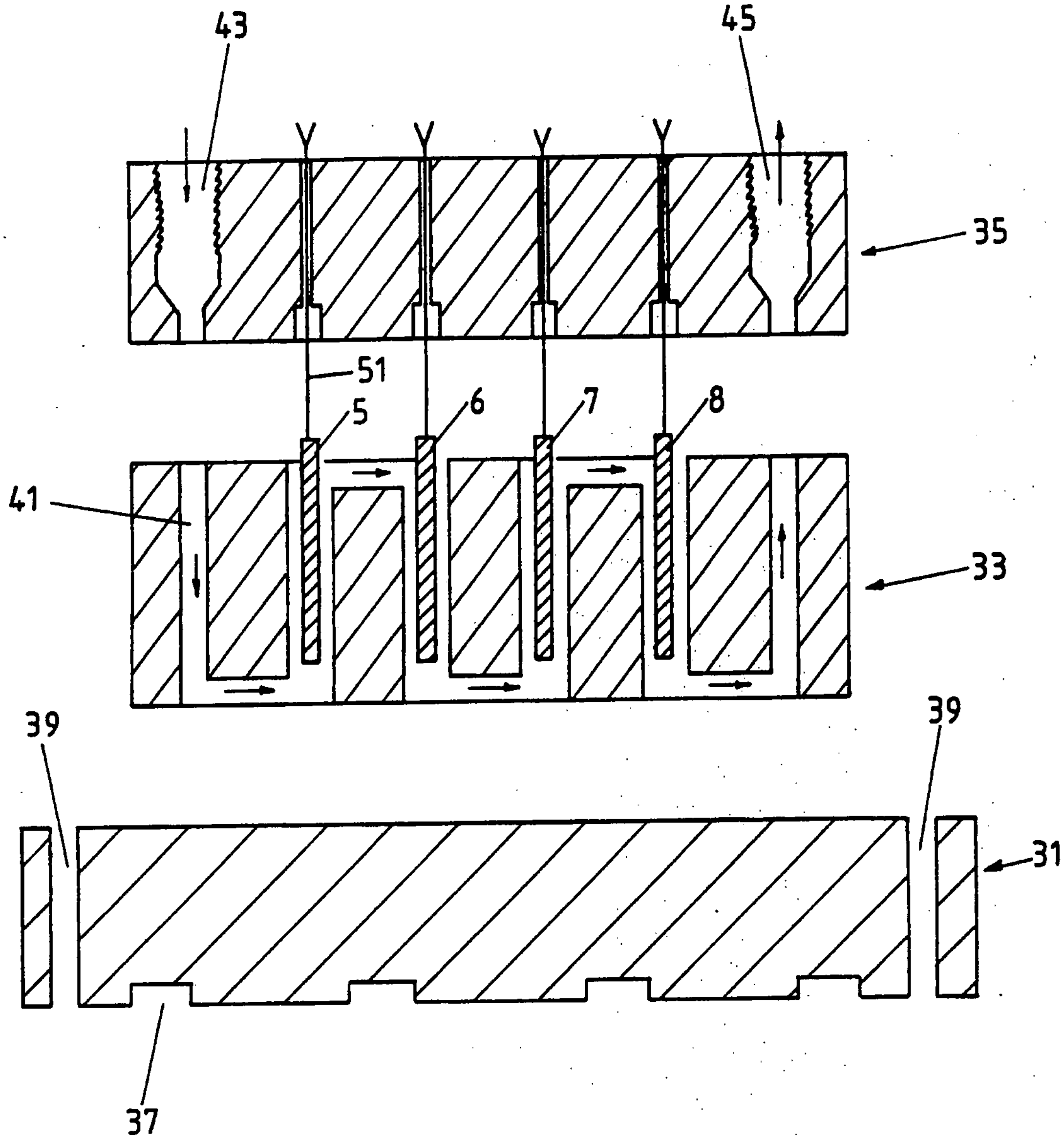

FIG. 2

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 90/01611

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC5: G 01 N 25/22

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
IPC5	G 01 N

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category *	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
X Y	DE, A1, 3102330 (KRAUSS, RALF) 26 August 1982, see page 5, line 13 - line 29; page 7, line 6 - line 11; page 9, line 8 - line 25 --	1-2,5 3,4,6-10
X Y	GB, A, 1498989 (MESSER GRIESHEIM GMBH) 25 January 1978, see page 2, line 30 - line 57; page 2, line 122 - page 3, line 3 --	1-2,5 3,4,6-10

* Special categories of cited documents: [10]

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"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
24th January 1991	08. 02. 91
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	Natalie Weinberg

Form PCT/ISA/210 (second sheet) (January 1985)

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	GB, A, 812607 (ROBERTSHAW - FULTON CONTROLS COMPANY) 29 April 1959, see page 1, line 45 - line 64	1-10
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A	US, A, 4835108 (MARSHALL H. COOPER) 30 May 1989, see column 1, line 64 - column 2, line 13	1-10
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ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.PCT/GB 90/01611

SA 41384

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 28/12/90
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-A1- 3102330	26/08/82	NONE	
GB-A- 1498989	25/01/78	AT-B- 344133	10/07/78
		BE-A- 832753	16/12/75
		CH-A- 582358	30/11/76
		DE-A- 2441857	18/03/76
		FR-A-B- 2283436	26/03/76
		NL-A- 7510235	02/03/76
		SE-A- 7509623	01/03/76
GB-A- 812607	29/04/59	US-A- 2922700	00/00/00
US-A- 4835108	30/05/89	AU-B- 596162	26/04/90
		AU-D- 7106287	04/02/88
		EP-A- 0255197	03/02/88
		JP-A- 63037250	17/02/88

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